Infrared Spectra of Charge Transfer Complexes between Zinc-Phthalocyanine and Vaious Amines (Commemoration Issue Dedicated to Professor Rempei Gotoh On the Occasion of his Retirement)

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Infrared Spectra of Charge Transfer Complexes between Zinc-Phthalocyanine and Various Amines

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The infrared spectra of the intermolecular complexes between zinc-phthalocyanine and various amines have been examined in crystalline state.

The absorptions by fundamental vibrations of aromatic amines were observed to shift to higher frequency region whereas those of aliphatic amines tended to decrease in the frequencies. The spectral changes of dimethyl sulfoxide indicated that the molecule bonded through oxygen atom. No significant changes were observed on the spectra of zinc-phthalocyanine even when the complex was formed.

INTRODUCTION

Phthalocyanine compounds have been widely studied as stable pigment materials, organic semiconductors, simple assimilated model for biological substance and catalyses. These powderly compounds are also known to show polymorphic behavior, that is, the appearance of more than two crystal forms, some of which is more stable than the other. The less stable α-form tansforms into the more stable β-form by heat treatment or by being dispersed in organic solvents. A stepwise mechanism of the transformation of copper-phthalocyanine in various organic suspension media had been observed by x-ray diffraction and electron microscopy by Suito and Uyeda.[1] When the experiment was extended to similar systems of the organic suspension with the zinc-phthalocyanine, some solvents produced unusual crystal phases whose crystal habits and structures greatly differed from the ordinary crystal phases such as the α- and β-forms.

These new crystals obtained were determined by the present authors[2] to be stoichiometric molecular complexes of zinc-phthalocyanine produced with solvent molecules such as aliphatic amines and aromatic amines which had all strong electron donating property due to the non-bonding lone pair. McCartin[3] showed that zinc-phthalocyanine played the part of the electron donor for strong acceptors such as 2, 4, 6-trinitrotoluene, sym-trinitrobenzene, and 2, 4, 7-trinitro-9-fluorenone in solution by means of spectroscopy. On the contrary, the solvent molecules which have the ability to form complexes with zinc-phthalocyanine are all electron donor and consequently the zinc-phthalocyanine was assumed to act as the electron acceptor. In the present study, infrared spectroscopy was applied to the crystalline complexes in order to examine the nature of the intermolecular bonding between zinc-phthalocyanine and amine by inspecting their spectral changes obviously caused by the complex formation.

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EXPERIMENTAL

1. Preparation of the Samples

The zinc-phthalocyanine (Fig. 1) was synthesized by a direct reaction of pure zinc dust and phthalonitrile. The crude products were purified first by washing for 24 hrs. with pure acetone in a Soxhlet extractor and then by repeated sublimation under the nitrogen atomosphere. The resulting needle-like crystals were converted into a finely divided powder by the acid paste method. About 0.1 g of the powder was dispersed in 10 ml of each solvent and kept at 50°C for 48 hrs. The precipitates were separated from the individual media by filteration and were dried under reduced pressure until the further changes of weight were not observed so that the adsorbed solvent molecules were eliminated as perfectly as possible.

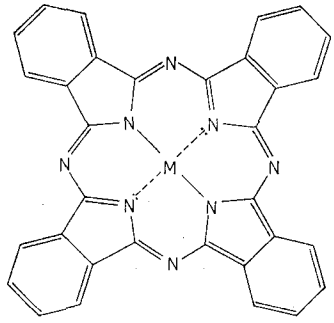

Fig. 1. Structure of the metal phthalocyanine molecule.

The organic suspension media adopted in the present work were pyridine, 2-methyl-pyridine (α-picoline), 4-methyl-pyridine (γ-picoline), 30% aqueous solutions of methyl amine, dimethyl amine, trimethyl amine, and D.M.S.O. all of which were commercial guaranteed grade and were used without any purification.

2. Analytical Procedures

The infrared absorption spectra of the specimens were recorded with a Perkin-Elmer Model 521 grating spectrometer. Since some of the complexes were found to decompose into their component materials in the process of pressing them into KBr disks, Nujol mulls were preferred in most of the cases. With pyridine complex as well as the pure polymorphs, KBr disks were also used since they were stable for the pressing. The spectra were recorded in the frequency region from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSIONS

1. The Effects of the Polymorphs on the Spectra

The infrared spectra of two polymorphs of pure zinc-phthalocyanine are shown in Fig. 2 (a), (b) where the spectral differences between two polymorphs can be clearly discriminated. It is well known that the changes in infrared ab-

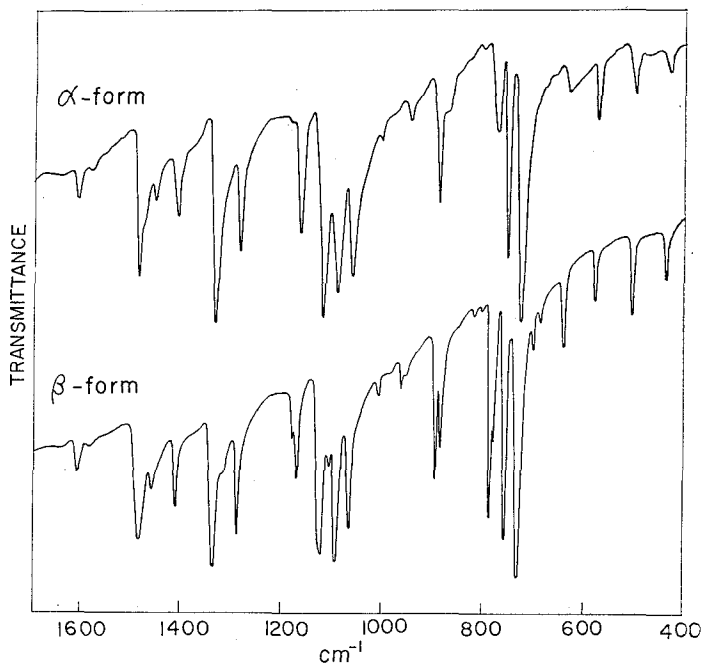

Fig. 2. Infrared spectra of the α-form (a) and the β-form (b) of pure zinc-phthalocyanine.

sorption of the same materials are caused not only by the changes of state but also, when the materials are in solid state, by the difference in its crystal phase. Such spectral change associated with the polymorphic modification of crystalline materials was reported by Hunt, Wishered and Bonham and also by other authors[4] with respect to inorganic substances. It was also reported by Ebert and Gottlieb[5] that the organic compounds including zinc-phthalocyanine which showed the polymorphism caused the spectral differences. Kendall[6] discussed the spectral differences in two copper-phthalocyanine polymorphs on the basis of the molecular arrangement in crystal. The spectral differences among three polymorphs of metal-free phthalocyanine was reported by Sharp and Dardon[7] and discussed in terms of the different stacking of the planar molecules.

As to zinc-phthalocyanine the most remarkable difference is the disappearance of the next eight bands in the spectrum of the α-form, 678, 693, 781, 877, 955, 1102, 1124, and 1172 cm^{-1}, all of which can be observed in the spectrum of the β-form. Another difference in the absorption frequencies is also conspicuous as listed in Table 1. The differences of infrared spectra among four polymorphs of zinc-phthalocyanine, including two new polymorphs other than the α and β-forms, were reported by the present authors[8] and will be published elsewhere with other crystallographic data based on x-ray and electron diffraction.

2. Complexes with Various Amines

The infrared absorption spectra of the complexes with pyridine, α-picoline and γ-picoline are shown in Fig. 3 (c), (d) and (e). The spectrum (a) is that

Table 1. Infrared Absorption Frequencies of Zinc-Phthalocyanine and its Amine Complexes.

Pure zinc-phthalocyanines		Zinc-phthalocyanine in complexes with amines						
α-Form	β-Form	Pyridine	α-Picoline	γ-Picoline	Methyl amine	Dimethyl amine	Trimethyl amine	D.M.S.O.
418	422	420	420	420	419	420	420	417
430	436	430	434	428	437	440	435	436
500	500	498	500	495	500	500	500	500
573	573	570	572	570	572	572	572	570
631	635	630	634	633	632	632	632	632
	665		667	665				665
	678	675	680		677	677	677	
	693	690	690		692	693	691	
721	729	720	722	716	727	729	725	727
750	752	747	750	750	750	750	750	750
768	773	770	770	766	770	770	768	776
	781				778	780	776	784
798	798							
865	870	864	867	860	863	864	863	875
					869			
	877				880	895		879
885	888	883	888	883	886	887	885	885
940	947	940	938	936				946
	955				952	951	950	960
1000	1003	1000	1000	1003	1003	1003	1003	1002
1056	1060	1056	1060	1058	1060	1061	1060	1058
1086	1089	1084	1087	1090	1090	1091	1091	1091
	1102							
1113	1117	1110	1115	1115	1115	1115	1115	1114
	1124							
1160	1162	1160	1164	1160	1164	1167	1165	1162
	1173				1180	1180		1165
1280	1284	1280	1282	1280	1282	1285	1283	1283
	1310				1310			1310
1330	1333	1327	1330	1330	1330	1332	1330	1328
1406	1409	1405	1410	1405	1407	1407	1407	1406
1450	1450	1449		1445	1450	1450	1450	1450
				1453		1465	1460	
1470	1470	1470	1470	1475				
1480	1481	1480	1485	1483	1481	1480	1482	1482
1580	1580	1580		1583	1580	1580	1580	1580
1604	1605	1604	1605	1610	1603	1603	1605	1603
							1607	

for the α-form reproduced schematically for comparison. Most of the bands shown in Fig. 3 and listed in Tables 1 and 2 nearly coincide with those of pure zinc-phthalocyanine and with some of the characteristic bands to the amines

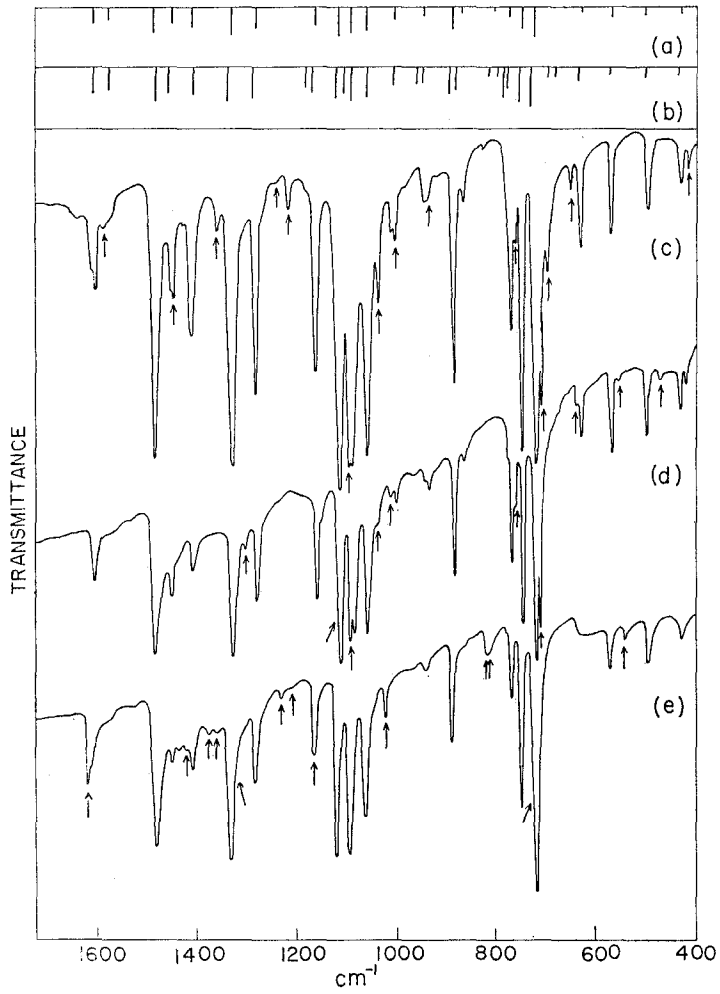

Fig. 3. Infrared spectra of zinc-phthalocyanine-amine complexes. (a), (b)=pure zinc phthalocyanines of the α- and β-form, (c)=pyridine, (d)=α-picoline, (e)=γ-picoline.

such as pyridine, α-picoline and γ-picoline. Although many absorption bands due to each amine are covered by the strong bands of zinc-phthalocyanine because these aromatic amines resemble the parts of phthalocyanine molecule itself, some characteristic amine bands can be explicitly observed and have been marked by arrows in Fig. 3.

The absorption spectra of the complexes with aliphatic amines are also reproduced in Figs. 4 and 5 including the spectrum for dimethyl sulfoxide complex and all of their frequencies are shown in Tables 1~4.

3. Effects of Complex Formation on the Fundamental Vibrations of Amines

a) Heterocyclic Amines The spectra of the complexes with pyridine, α-picoline and γ-picoline were characterized to be composed of the spectrum of zinc-phthalocyanine and that of each amine. Since many of the bands ascribed to amines

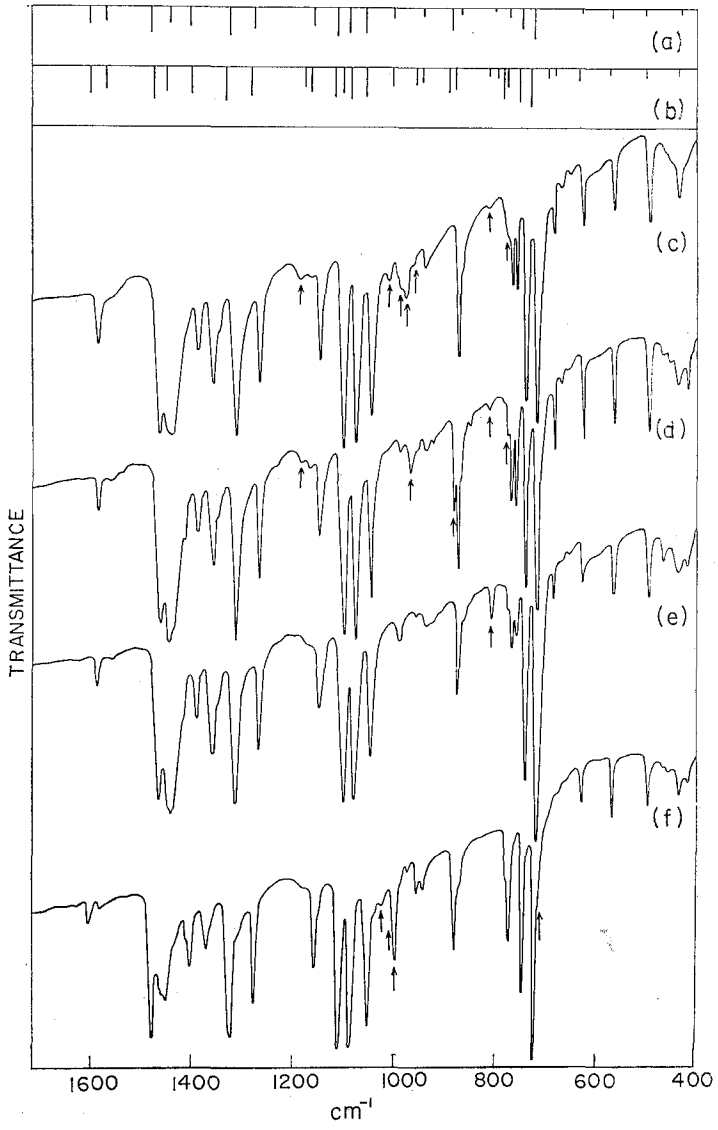

Fig. 4. Infrared spectra of zinc-phthalocyanine-amine complexes. (a), (b)=pure, zinc-phthalocyanines of the α- and β-form (c)=methylamine (d)=dimethylamine, (e)=trimethylamine, (f)=D.M.S.O.

overlie those of the zinc-phthalocyanine, only the frequencies of these adduct molecules which can be clearly distinguished are listed in Tables 2~4. Although the assignments of infrared absorption bands for aromatic amines were so far reported by many investigators in regards to the complexes with halogens and metal halides, Long's assignments[9] based on a normal co-ordinated calculation were reliable for pyridine and γ-picoline. On the basis of a similar theoretical calculation, Green[10] also proposed the assignments for the fundamental vibrations of α-picoline, γ-picoline and pyridine. The assignments for amines which

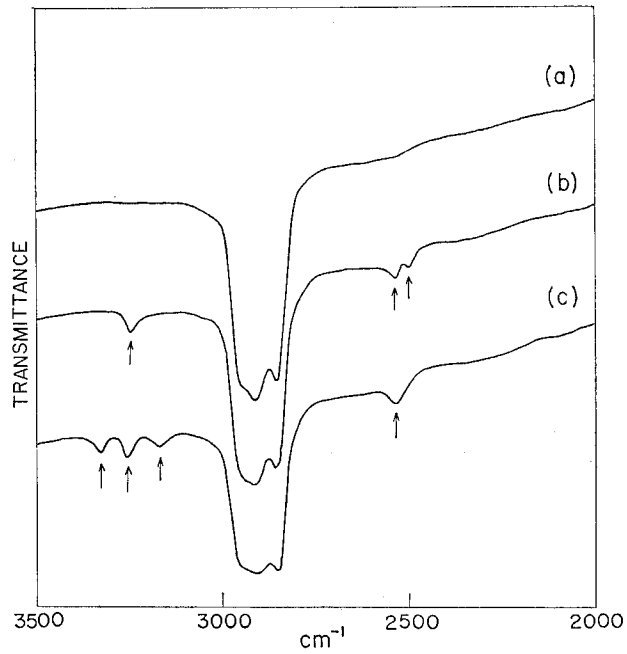

Fig. 5. Infrared spectra of zinc-phthalocyanine-amine complexes from 2000 to 3500 cm^{-1}. (a)=trimethylamine, (b)=dimethylamine, (c)=methylamine.

Table 2. Infrared Absorption Frequencies of Amines in the Complexes with Zinc-Phthalocyanine and those of the Free Amines.
* Goldstein and Mooney. Ref. (4)

ZnPc ·Py	Pridine	$CuCl_2$* ·2Py	ZnPc ·αPic	α· Picoline	$CuCl_2$* ·2α·Pic	ZnPc ·γ·Pic	γ· Picoline	Assignment	
420	405	444							16 b
			474						
			494	470	481			φ(C-C)	11
648	605	645	557	548	559	539	514	ring	6 a
700			640	629	652			α(C-C-C)	6 b
711	700	691	715	700	699			φ(C-C)	11
760	749	764				743	728	φ(C-C)	4
						810			
						816	801		12
935	891	876	774	751	768 783			γ(CH)	10 a, 10 b
1008	992	1009	1015	994	1033	1019	994	ring	1
1035	1030	1042							12
			1035	1040	1044			β(CN)	18 a
1092	1085	1063	1095	1099	1075	1165	1090	β(CH)	18 b
						1215	1212		13
1215	1218	1218	1126	1143	1155	1230	1220	β(CH)	9 a
1235									
1355	1288	1240	1303	1291	1310	1334 1355	1289	β(CH)	3
						1373	1365	ν(CN)	14
1442	1439	1449				1420	1417	ν(CN)	19 b
1596	1583	1596				1618	1604	ν(CC)	8 a

Table 3. Infrared Absorption Frequencies of Aliphatic Amine in the Complexes with Zinc-Phthalocyanine and those of the Free Amines.

ZnPcMeAm	MeAm	ZnPc2MeAm	2MeAm	ZnPc3MeAm	3MeAm	Assignment
785	783	786				
825		825	881			δNH
		895				
980						
990						ρCH_3
995						
1025	1045	983	986	820	826	νCN
		1035	1034			
		1200	1176			CH_3
1200	1127					ωNH_3
3170	3361	3230	3315			νNH
3260		3250				
3320	3427					

Table 4. Infrared Absorption Frequencies of free D.M.S.O. and those in the Complex.

Zn·Pc·D.M.S.O.	D.M.S.O.	Assignment
718	690	C−S Stretching
1002	1055	S=O Stretching
1005		
1029	1012	CH_3 Rocking

appeared in the complex spectra are also shown in Table 2 according to these references. Most of the absorption bands of the amines in complexes showed more or less increases in frequency. Particularly, significant shifts were observed for the ring deformation modes when the amine was co-ordinated to a metal as reported by McWhinnie,[11] Clark and Williams[12] and Brown *et al.*[13] In every case, the frequencies of the ring deformation vibration of aromatic amines were always observed to shift to higher frequency region on complex formation. This effect was also well detected in the present study as shown in Table 2 for the complexes with aromatic amines. Such increases in absorption frequencies due to complex formation are the general tendency of the spectra of molecules acting as electron donor in complexes being referred to as the "tightening up" effect. For instance, the example of such blue shift was also reported by Goldstein and Mooney[14] with respect to pyridine which formed complexes with $CuCl_2$ and $CuBr_2$ and their results are also listed in Table 2 for comparison. As to the configuration of these copper halide complexes, the nitrogen atom of pyridine molecule is known to be directly bound to copper ion. From the similar tendency to the frequency shifts of amines, it was inferred that the aromatic amines studied here were also directly bound to the central zinc ion of the phthalocyanine derivative with nitrogen in the heterocycles as a ligand. The spectral change of zinc-phthalocyanine itself caused by complex formation will be discussed in later section.

b) Aliphatic Amines As KBr disk method was not applicable to the complexes

of zinc-phthalocyanine with aliphatic amines because of their instability against the pressing into KBr disks, Nujol mulls were used for these complexes to record the infrared spectra. Consequently, the absorption bands by C-C or C-H vibrations of aliphatic amines in complexes were covered completely by the strong absorption bands of Nujol. On the other hand, however, the bands due to C-N or N-H vibrations in amines were neither interfered by Nujol nor by zinc-phthalocyanine. It is well known that the absorption bands due to N-H stretching vibrations in methyl and dimethyl amines shift to lower frequency region when coordinated to metal ions. These shifts were also observed in the spectra of complexes with zinc-phthalocyanine as shown in Fig. 5 and Table 3. The assignments for methyl amine, dimethyl amine and trimethyl amine have been reported by Cleaves and Playler,[15] Buttler and McKean,[16] and Barcello and Bellanato[17] respectively. Their results were used in the present investigation though these reports were mainly concerned with the gas phase amines. It can be easily seen in Table 3 that the C-N stretching vibration of each amine in the complex showed the absorptions at lower frequency region than that for the free amines. These changes of absorption frequencies were regarded as a result of charge transfer from nitrogen of amines to zinc-phthalocyanine, because such a charge transfer effect causes the decrease in the bond order of C-N and N-H bonds. The electron donating ability of amine is mainly due to the non-bonding lone pair electrons of nitrogen. Therefore, all of the amines in complexes with zinc-phthalocyanine were considered to be bound to zinc-phthalocyanine with the nitogen as ligand in the same way as the aromatic amines.

c) **Dimethyl Sulfoxide (D.M.S.O.)** As to the spectra of the complexes with dimethyl sulfoxide, most interesting band is that due to the S=O stretching vibration, since this band should be most informative on the structure of the intermolecular bonding between zinc-phthalocyanine and D.M.S.O. There appeared three distinct bands which were assumed to be due to D.M.S.O. in the spectrum of the complex. The strongest one was observed at 1002 cm^{-1} with a shoulder at 1005 cm^{-1} and both absorptions were assigned to S=O stretching vibrations. Pure D.M.S.O. shows a very strong absorption at 1028 cm^{-1} with a shoulder at 1045 cm^{-1} by S=O stretching according to the assignments proposed by Cotton.[19] Another strong band which appeared at 718 cm^{-1} as a shoulder of the strong band of zinc-phthalocyanine in the complex at 727 cm^{-1} was considered to be due to C-S stretching which was reported by Cotton to appear at 698 cm^{-1} with large intensity and shifted to about 730 cm^{-1} by complex formation with $SnCl_4$. The third band at 1029 cm^{-1} was assingned to CH_3 rocking vibrations. There exist two possibilities as to D.M.S.O. for connecting to metals or metal complexes. One possibility is a connection by the way of the sulfur atom and the other is by oxygen. In the former case, S=O stretching frequency should show the tendency to increase and in the latter case, the decrease in the absorption frequency can be expected by considering the electronic nature of the S=O linkage as has been reported by Cotton *et al.* When this criterion was taken into account, it is easily concluded that the oxygen atom, which has also a lone pair electrons, partici-

pates in the intermolecular bonding in the complex of D.M.S.O. with zinc-phthalocyanine, since the S=O stretching bands at 1045 cm^{-1} of D.M.S.O. was greatly shifted to 1000 cm^{-1}.

4) The Spectral Changes of Zinc-Phthalocyanine by Complex Formation

Although the spectrum of zinc-phthalocyanine more or less suffered the changes by complex formation, the changes are not so large that the spectra could be regarded as similar to one of the original spectra of the α-form or the β-form of pure zinc-phthalocyanine. As noted above, the spectrum of the β-form shows a strong absorption at 781 cm^{-1} whereas such a band is not observed with the α-form. Moreover the β-form has two sets of sharp doublet bands at 877; 888 and 1162; 1173 cm^{-1} though the α-form shows corresponding bands only at 885 and 1160 cm^{-1} respectively. The absorption bands at 1102 and 1124 cm^{-1} are also characteristic to the β-form. When the complexes of zinc-phthalocyanine with n-donor molecule absorbed near 877 and 888 cm^{-1}, or 1162 and 1173 cm^{-1}, the spectrum was designated as a β-like spectrum and when the spectrum has no absorption peaks at these frequencies, the spectrum was named as a α-like one. According to this criterion, the complexes with pyridine, α-picoline, γ-picoline and trimethyl amine give rise to the α-like spectra whereas methyl amine and dimethyl amine produced the complexes which showed the β-like spectra, although slight frequency shifts were, of course, observed in every spectrum. The spectrum of zinc-phthalocyanine complex with D.M.S.O. shows the character of the β-form. The common aspect to all spectra of the complexes is the disappearance of absorption bands at 1102 cm^{-1} and 1124 cm^{-1}, the characteristics to the β-form phthalocyanine. Even the β-like spectra though classified as above can be referred to as being α-like so far as this band is concerned. Such a characteristic feature of the spectra arising from the complex formation as showing the α-like one rather than the β-like suggests that the inter molecular forces of the parallelly stacked phthalocyanine molecules themselves were weakened by the relaxation of molecular stacking arising from the insertion of donor molecules between them, since the α-form is known to be less stable energetically than the β-form crystal, assuming different stacking of the planar molecules.

CONCLUSION

The infrared spectra of the n-donor complexes of zinc-phthalocyanine clearly indicated that both aromatic and aliphatic amines were bonded to zinc-phthalocyanine with the nitrogen atom by donating their non-bonding lone pair electrons. The complex of D.M.S.O. appears to be bound with oxygen atom.

The vibrational frequencies of aliphatic amines fall off as the complex is formed whereas those of aromatic amines show the tendency of blue shift which was assumed to be due to tightening-up effect of the pyridine ring.

As deduced from the infrared spectrum and the result of x-ray analysis of the β-form crystal, it is likely that the strong interaction among the zinc-phthalocyanine molecules is relaxed on complex formation and consequently the

spectra became alike to that of the α-polymorph.

The samll spectral changes of zinc-phthalocyanine suggest that the position where the n-donor molecules are attached is not the macrocyclic ring of phthalocyanine but the central part of zinc-phthalocyanine *i.e.* zinc ion itself.

Any significant spectral change, therefore, may be anticipated to appear in the far-infrared region where the absorptions due to zinc-ligand, pyrrole ring vibration, and donor molecule-phthalocyanine bond are regarded to occur.

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